Combining Bio- and Chemo-catalysis for the Conversion of Bio-Renewable Alcohols

Marr, A. C. (2015). *Combining Bio- and Chemo-catalysis for the Conversion of Bio-Renewable Alcohols*. Paper presented at International Symposium on Green Chemistry 2015, La Rochelle, France.

Combining Bio- and Chemo-catalysis for the Conversion of Bio-Renewable Alcohols

Trends Biotech. 2011, **29**, 199–204

Catal. Sci. Technol., 2012, **2**, 279-287

Andrew C. Marr, Queen's University Belfast

3rd ISGC, La Rochelle, France, May 2015.

Biomass and Bio-Renewables

- Renewables industries must be sustainable businesses and able to operate competitively without subsidy.
- **Biomass** is ubiquitous, as human's need to grow food.
- Promising substrates are food and agricultural wastes.
- Similar to oil, biomass is a potential source of energy and chemicals.
- The economics of biomass utilisation depend upon the extent to which value added products are produced.
- In EU FP7 project GRAIL we are looking at utilising biodiesel waste for further energy and chemicals.

GRAIL FP7: Valorising Biodiesel Waste

Energy and chemicals from waste: recycled cooking oil

Fats & Oils $\longrightarrow$ Liquid Fuel

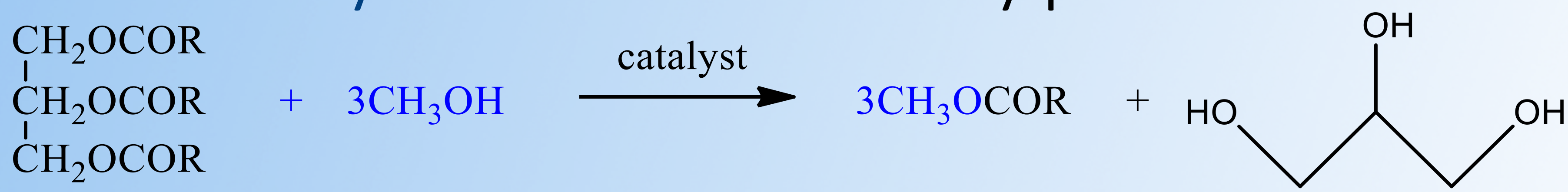
- **Biodiesel** is produced in large volume in the EU.
- In some cases the input is **used vegetable oil**.
- Energy from waste.
- 160, 000 tons/anum (per plant).
- Reducing pollution.
- Recycling chemical energy.
- Not atom-efficient…

http://www.grail-project.eu
9 countries, 15 partners

GRAIL
Glycerol Biorefinery Approach for the Production of High Quality Products of Industrial Value

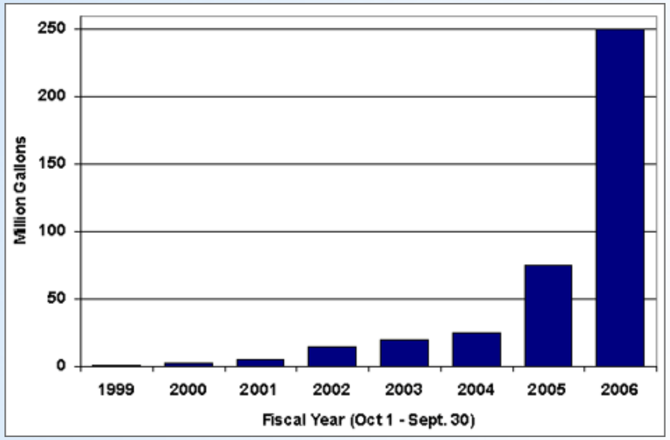
The Problem with Biodiesel

Glycerol is formed as the by-product



- Approx. 10% is **crude** glycerol.
- Crude glycerol is of low value [in 2010 about 20 times less than purified glycerol].
- Glycerol has potential uses in chemicals and energy.
- But purification is expensive.
- Much of the glycerol could go unused (become waste).
- Crude glycerol must be used.
- Whole cell biocatalysis.

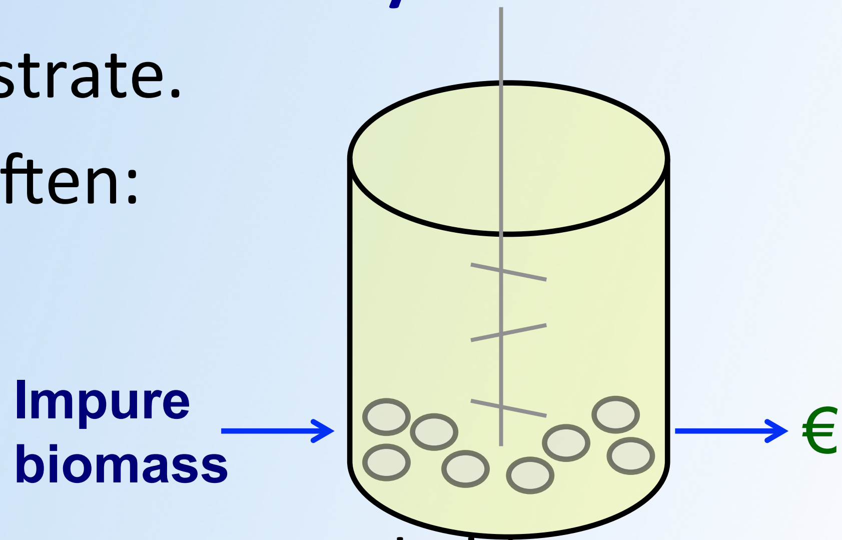
Increase in biodiesel



US biodiesel sales: US Dept. Energy

Using Whole Cell Biocatalysis.

- Crude biomass is a difficult substrate.
- Bio-renewable substrates are often:
  - Impure
  - Oxygenated
  - Aqueous



- Petrochemical catalysts tend to convert crude biomass unselectively and become poisoned.
- One solution is whole cell biocatalysis.
- Micro-organisms live on biomass and enrich the aqueous growth medium in a chemical.
- Chemicals produced depend on metabolic pathways
- Coupling whole cell biocatalysis to chemocatalysis provides routes to many other chemicals.

Combining Bio and Chemo-Catalysis

The Biorefinery Concept: **Fuels and chemical products from biomass.**

We are combining whole cell biocatalysis with chemocatalysis in order to transform waste into value-added chemicals

Whole cell biocatalytic fermentation + Chemocatalysis

- minimizing intermediate separations – intensification
- minimizing hazards

Biocatalysis: Whole Cell Fermentation of Glycerol

Dr Martin Rebros and Prof Gillian Stephens

Anaerobic Fermentation

Performance	Purified glycerol	Bio-diesel glycerol
Initial glycerol /g.dm^{-3}	18.8	19.1
Final 1,3-propanediol /g.dm^{-3}	9.7	10.2
Duration of fermentation /h	9.25	5.5
Productivity /g.dm^{-3}.h^{-1}	0.97	1.71
Productivity /Mol.dm^{-3}.h^{-1}	0.0064	0.0225

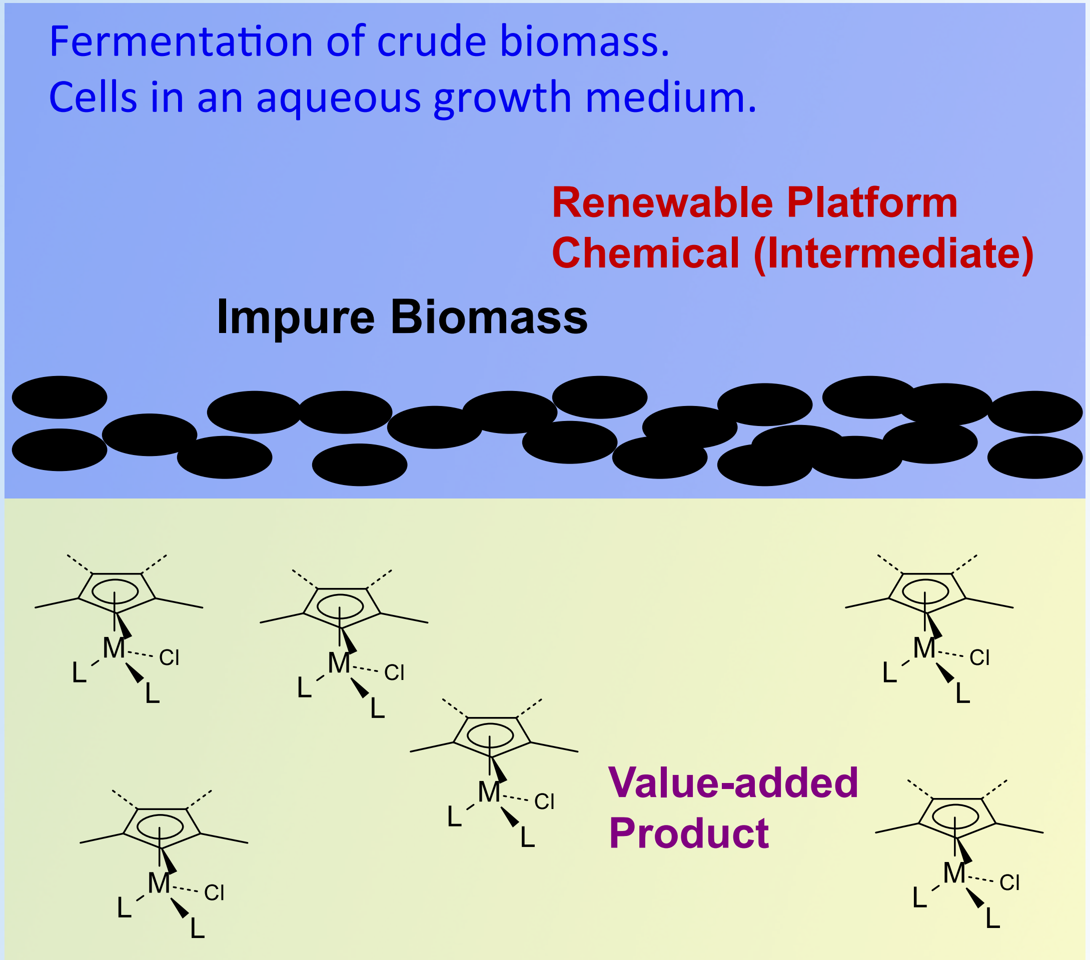
Chem. Commun. **2009, 2308 – 2310.** Further studies for GRAIL, Martin Rebros

Strategy to Utilize Crude Biomass Combining Bio- and Chemo-catalysis

Aqueous solution of a chemical intermediate.

Extract using Ionic liquid

..containing a Catalyst.



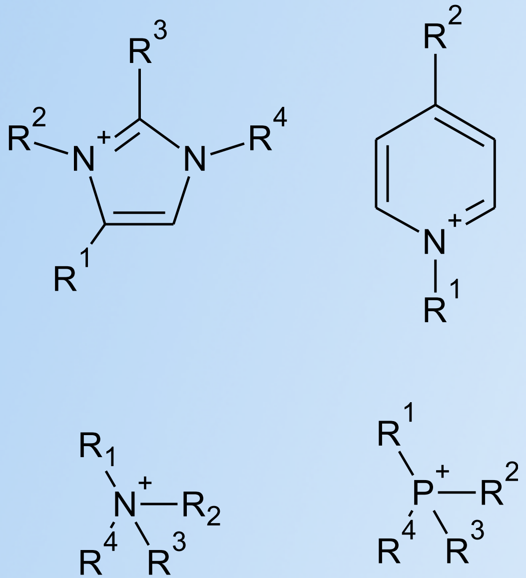
€/£

Trends Biotech. 2011, 29, 199–204

Ionic Liquids

- A salt that is liquid under reasonable temperatures
- Behaves as an **involatile polar solvent**
- Can change the cation and anion to tune properties.

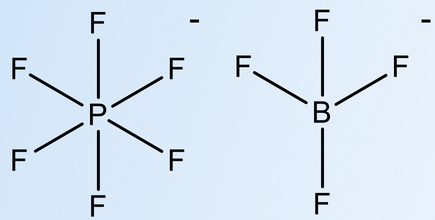
Cations

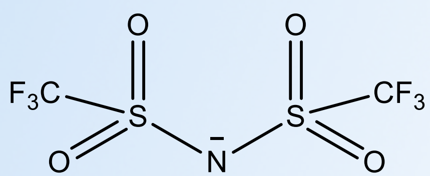


+ anions

Cl^-, Br^-, I^-

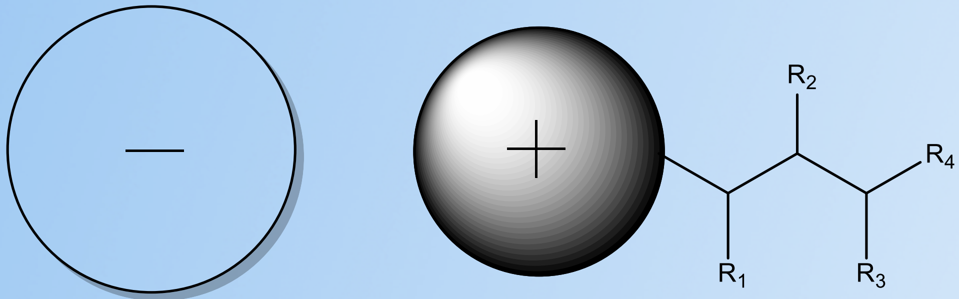
$CH_3CO_2^-$, $CF_3CO_2^-$, $CF_3SO_3^-$

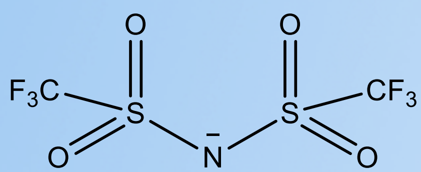




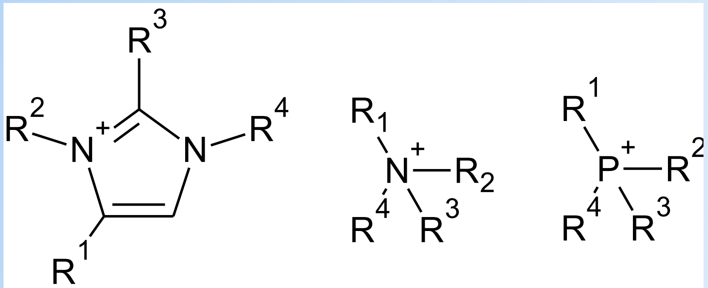
Ionic Liquids in Bio-Alcohol Processes

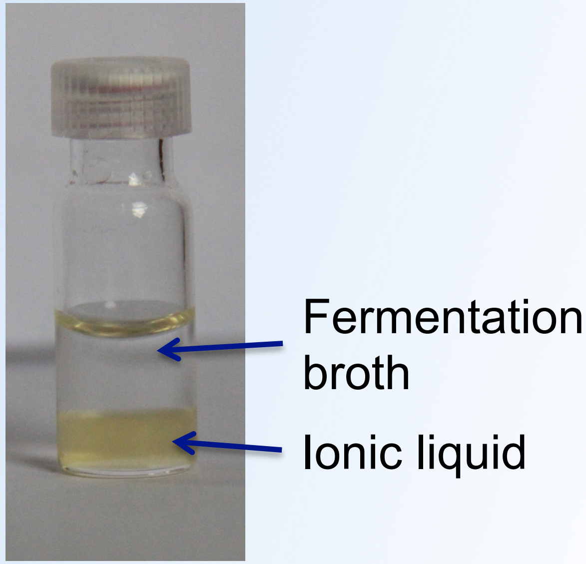
Ionic liquids have the potential to extract and transform bio-alcohols





Hydrophobicity



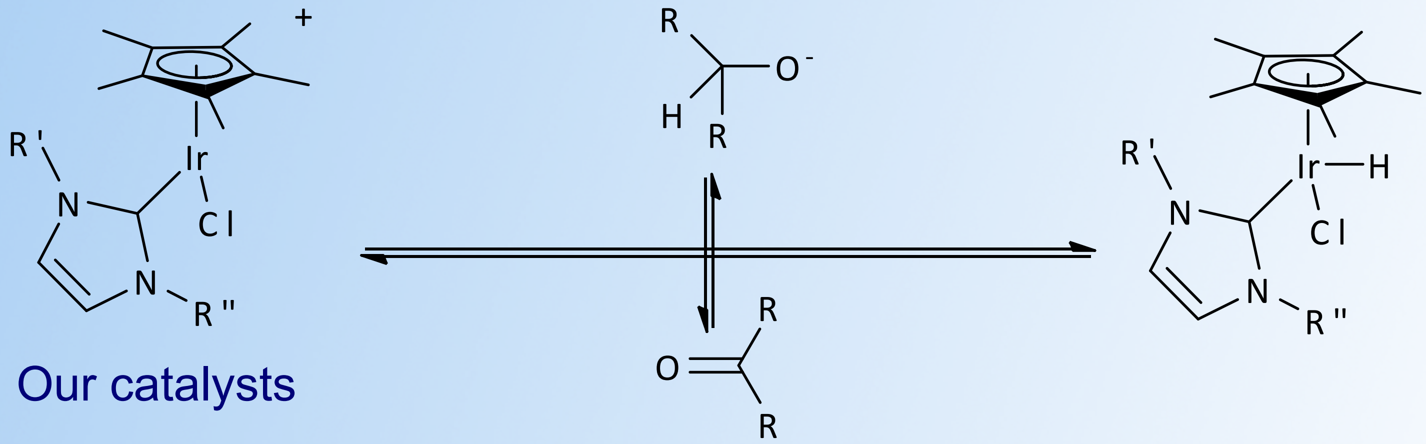


- Non-volatile, very high boiling solvents (comparable with sulfolane).
- Toxicity, biocompatibility, biodegradation can be varied.
- IL can be functionalized to suit a purpose e.g. hydrophobicity.
- Act like high polarity solvents, high affinity for alcohols.

Chemo-Catalysis on Bio-Alcohols

Hydrogen Transfer Reactions

- Aliphatic alcohols like 1,3-PDO are not highly activated for reaction
- Addition of a homogeneous catalyst can reversibly remove hydrogen
- Hydrogen transfer or hydrogen borrowing reactions enable transformation of bio-renewable alcohols under mild conditions
- Examples include amination, hydrogenation and dehydrogenation.

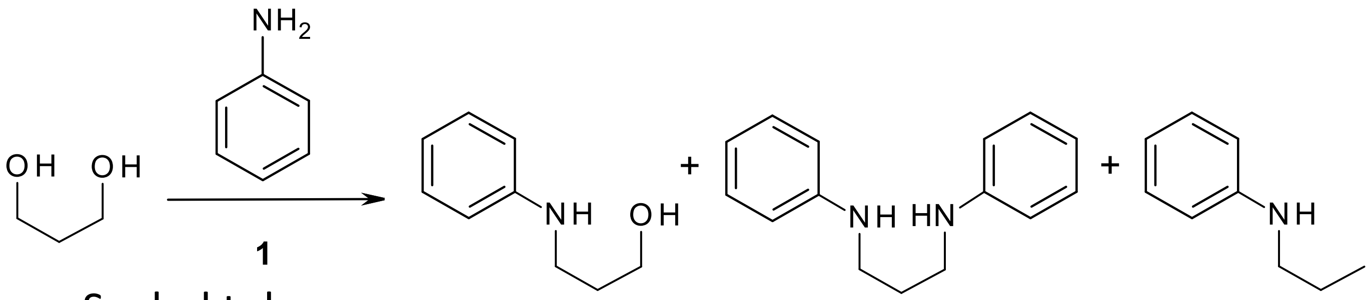


Our catalysts

Hydrogen Transfer literature: Bäckvall, Beller, Blum, Cole-Hamilton, Crabtree, de Vries, Grigg, Milstein, Morris, Peris, Vogt, Watanabe, Williams, Wills, Yamaguchi and others.

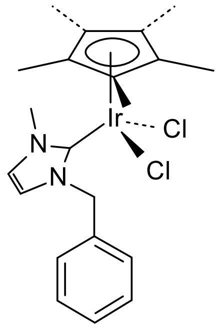
Review on renewable alcohols: A.C. Marr, *Catal. Sci. Technol.*, 2012, 2, 288 – 290.

Alcohol Amination in Ionic Liquid vs. Toluene



Sealed tube,
1 mol% catalyst, 24h

3 4 5

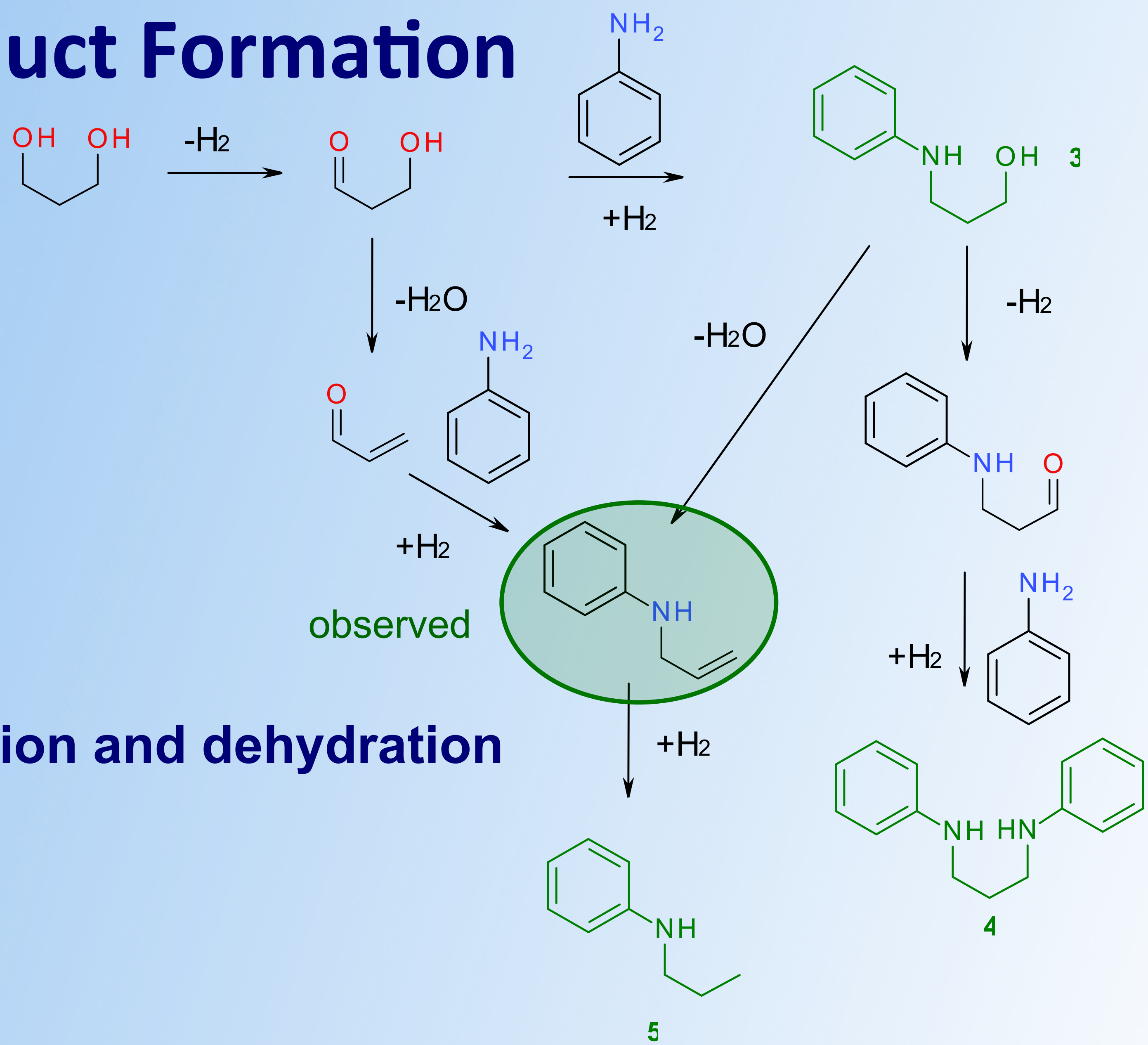


1

Solvent	Temp. / °C	Conversion /%	3	4	5
Toluene	115	>99	ND	65	35
$N_{1,8,8,8}NTf_2$	115	>99	14	43	43
Toluene	60	16	100	ND	ND
$N_{1,8,8,8}NTf_2$	60	>99	20	15	65
None	60	51	83	17	ND

- $N_{1,8,8,8}NTf_2$ is a good solvent for amination
- High tendency to form the amination + dehydration product (**5**)
- Supports **lower temperature activity** *Chem. Commun*. 2009, 2308 – 2310

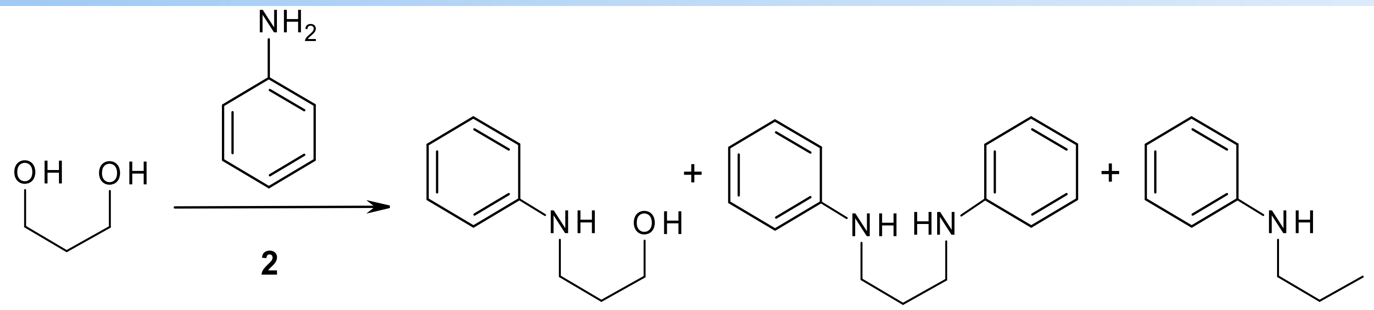
Product Formation



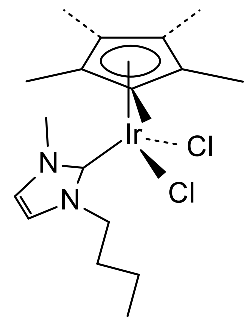
Amination and dehydration

- Dehydration occurred readily in the presence of catalyst **1**
- The ionic liquid promoted this pathway.

Amination in $N_{1,8,8,8}NTf_2$



$N_{1,8,8,8}NTf_2$, K_2CO_3 3 4 5



2

- Conducting the amination in $N_{1,8,8,8}NTf_2$ **3** is rarely observed.
- Selectivity could be controlled to yield **4** or **5**.

Temp /°C	1,3-PDO: aniline	Conv. /%	3	4	5
115	1:2	>99	ND	trace	>99
115	1:10	>99	ND	>99	ND

Prepared at concentration 0.2 moldm^{-3}, 48h

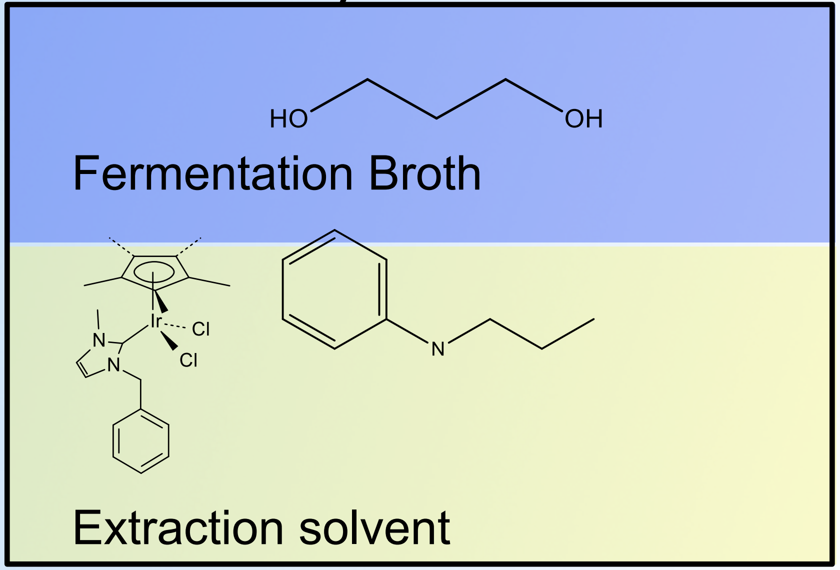
Catal. Sci. Technol., 2012, 2, 288 – 290

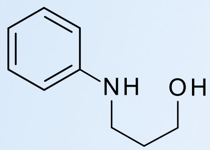
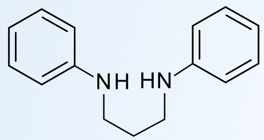
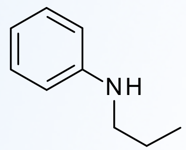
Sophie Lacroix

Combined Bio and Chemo-catalysis

EPSRC Engineering and Physical Sciences Research Council

- To the aqueous solution resulting from biocatalysis on crude waste glycerol we added:
  - Solvent $N_{1,8,8,8}NTf_2$ (or toluene)
  - Aniline
  - A hydrogen transfer catalyst
  - The base K_2CO_3
- and performed amination



Temp /°C	Time / h	Solvent	Convers. /%	Av. rate / $Moldm^{-3}h^{-1}$			
115	24	Toluene	20	0.008	82	18	ND
60	48	$N_{1,8,8,8}NTf_2$	12	0.003	ND	ND	100
42	48	$N_{1,8,8,8}NTf_2$	10	0.002	ND	ND	100

Liu, Rebros, Stephens and Marr, *Chem. Commun.* 2009, 2308 – 2310

Shifang Liu

Observations from Proof of Concept

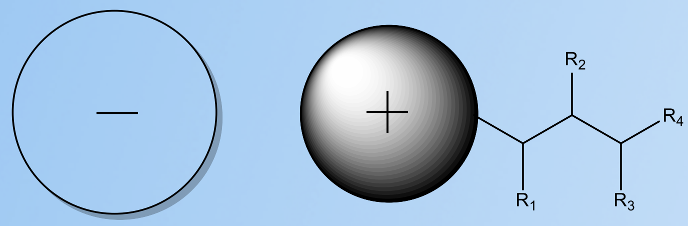
1. Coupled extraction and chemical conversion from fermentation broth is achievable with a catalyst in an ionic liquid.
2. Dehydration occurs readily in the presence of water in hydrophobic ionic liquids.
3. Low conversions as the extraction from aqueous solution with $N_{1,8,8,8}NTf_2$ was poor.

Action points

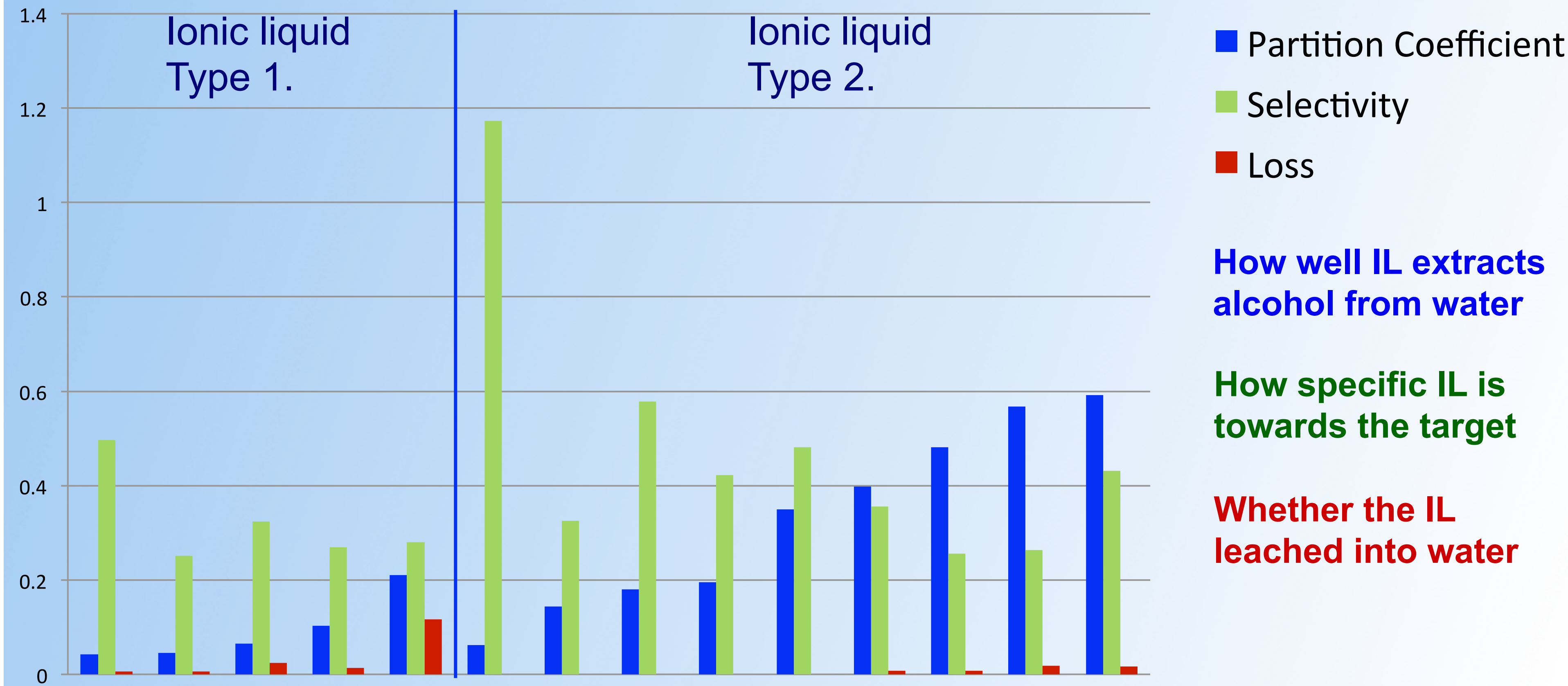
- Can we tune the ionic liquid and improve extraction?
- Can we run dehydration of bio-alcohols in an IL?

A.C. Marr, *Catal. Sci. Technol.*, 2012, 2, 279-287

ILs, Extraction of Diols from Water



Testing hydrophobic ILs for the extraction of polyols from water.

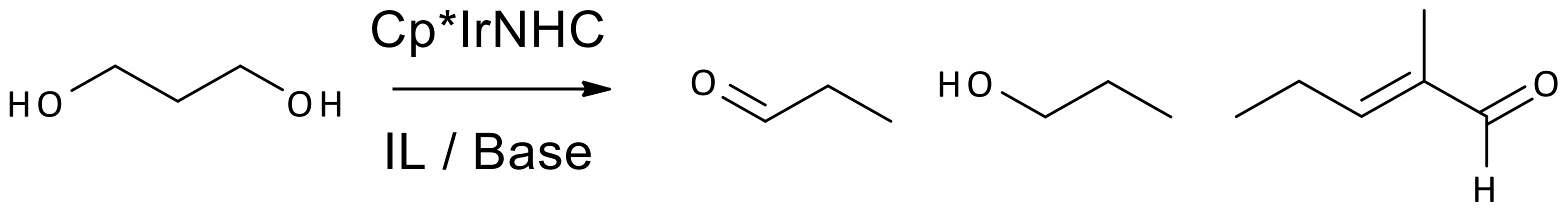


Extraction can be greatly improved by tuning the ionic liquid.

Xiaohan Liu

Hydrogen Transfer Initiated Dehydration: HTID

- Under hydrogen transfer conditions and employing catalysts **1** or **2** **dehydration** occurs, particularly in IL solvents.
- Can **dehydration** be carried out under mild conditions in the absence of an amine? **Yes**.

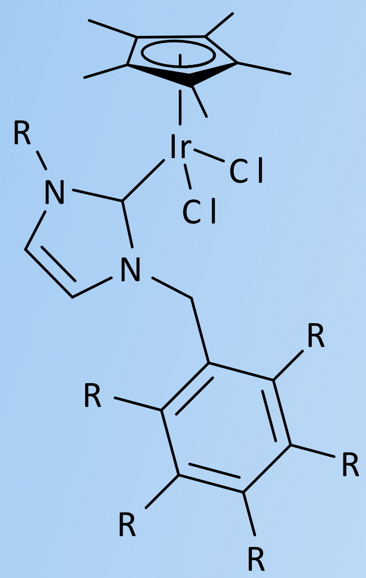


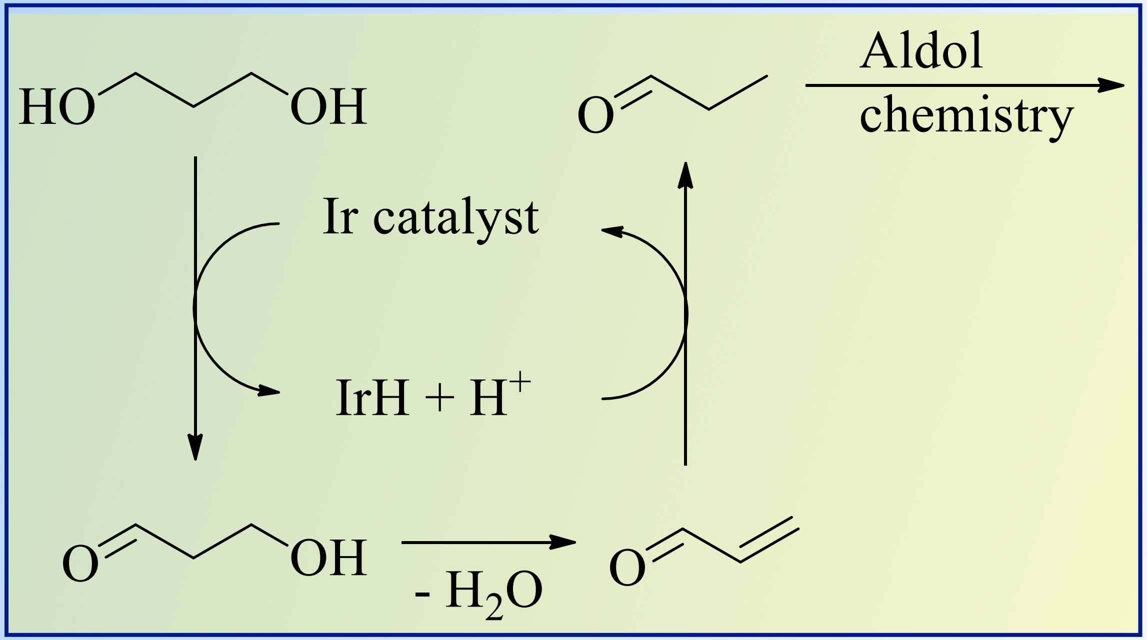
- Products are the result of coupled **hydrogen transfer** and **dehydration** reactions.
- The dehydration chemistry is initiated by metal catalyzed dehydrogenation.
- Aldehydes are required for a wide range of chemical applications

Catal. Sci. Technol., 2012, 2, 288 – 290

Thomas Eisenhart, Yueming Wang

HTID Reaction Pathway



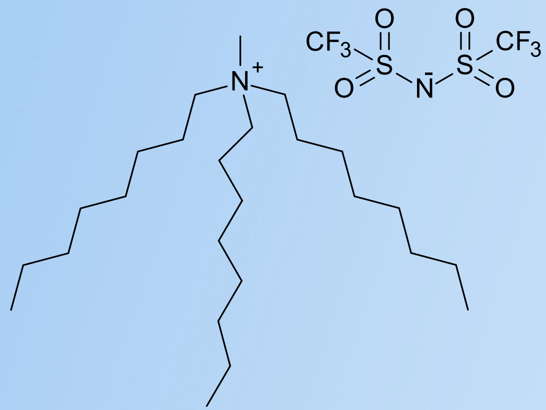


- In NTf_2^- ionic liquids dehydration was found to be facile.
- Dehydrogenation forms an *aldol*.
- The aldol readily dehydrates.
- The catalysts operate in air and in the presence of water.
- The Ionic liquid also boosts propanal selectivity and aids separation.

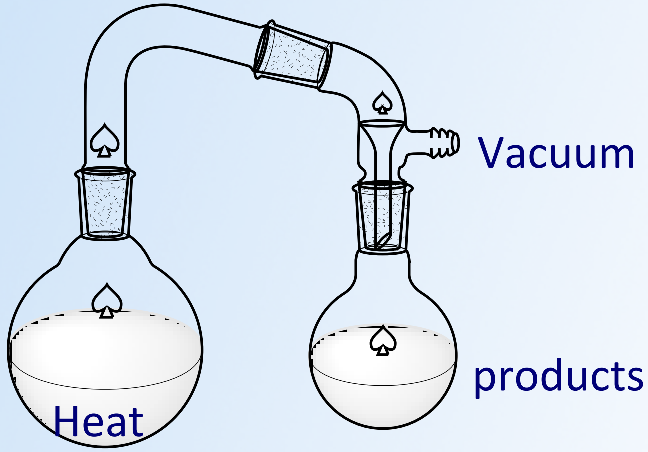
HTID in ILs, aldehyde isolation

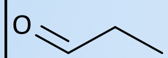
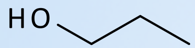
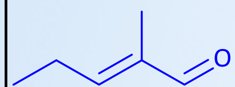
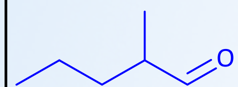
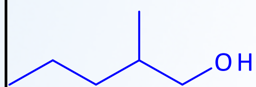
- The involatile nature of ionic liquids can be exploited
- Products are more volatile and can be distilled out.

IL



IL + substrate + catalyst

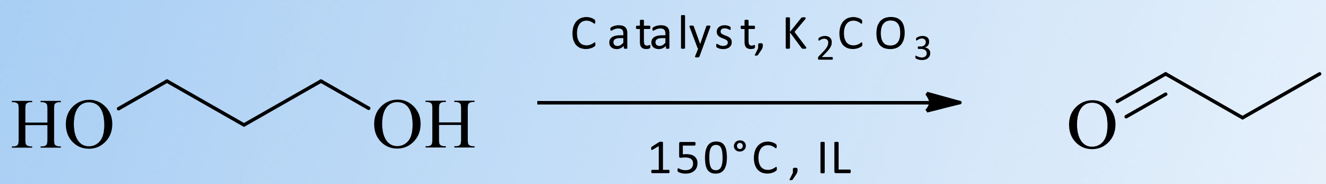


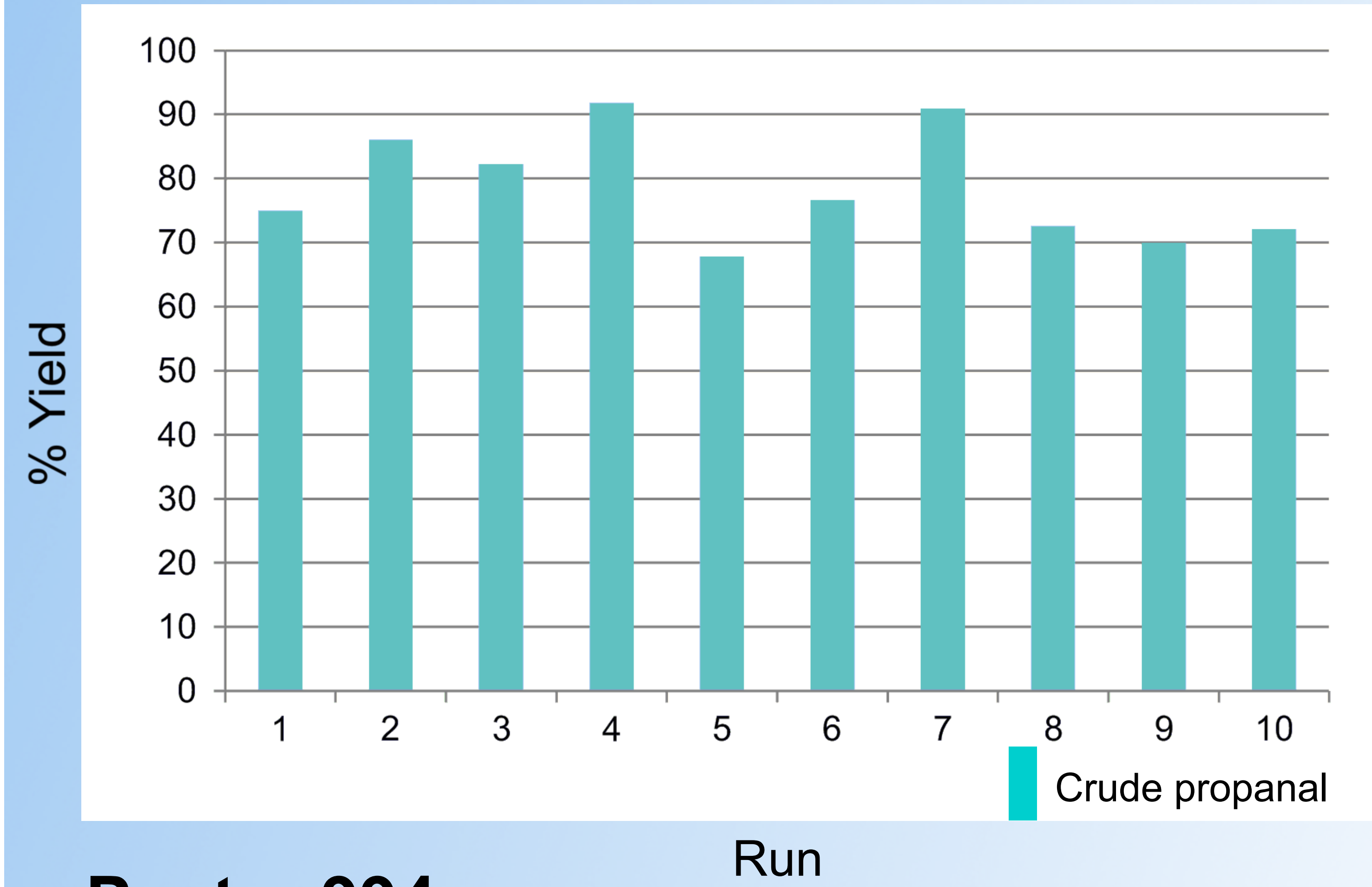
Solvent	Temp / °C	Time /h	Conv. / %					
Toluene[a]	110	48	92	15	9	39	10	26
$N_{1,8,8,8}NTf_2$[b]	110	30	100	80	6	8	3	trace[d]
$N_{1,8,8,8}NTf_2$[c]	140	24	**100**	**87**	3	3	trace	trace[d]

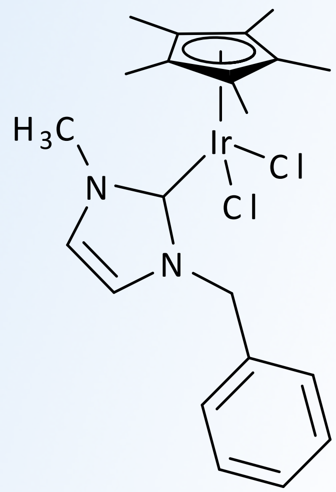
a. Sealed tube, catalyst 1 mol%, a+b: 0.35 bar; b. Catalyst 1 mol%;
c. Catalyst 0.5 mol%; a+b+c: products expressed as mol %.
d. Balance was acetaldehyde.

YueMing Wang

Optimising & Catalyst Recycling







Catalyst precursor

Poster 994

YueMing Wang and **Fabio Lorenzini**

Summary

- Combining Bio- and Chemo-catalysis to valorise bio-renewable waste streams.
  - Combining biocatalysis and chemocatalysis enables the valorisation of crude biomass waste
  - Whole cell biocatalysis converts crude biomass to diols
  - Ionic liquids can be tuned to extract bio-renewable alcohols from fermentation broth
  - Hydrogen transfer activates aliphatic alcohols
  - Addition of amine leads to amination (N-alkylation)
  - Operating in ionic liquid promotes dehydration to aldehydes
  - Ionic liquids enable facile removal of volatile products and catalyst recycling.

Acknowledgments

Homogeneous Catalysis

Dr Fabio Lorenzini, poster 994

Dr Ciara Pollock

Dr Shifang Liu

Yueming Wang

Thomas Eisenhart

Sophie Lacroix

Dr Graham Saunders, Waikato, NZ

Ionic liquids

Gerald Donnelly

Xiaohan Liu

Prof Ken Seddon, QUILL, UK

Dr Gosia (Małgorzata Swadźba-Kwaśny), QUILL, UK

Dr John Holbrey, QUILL, UK

Prof Pete Licence, Nottingham, UK

Gels

Dr Patricia C. Marr, QUB, UK

Dr Steven Craythorne

Viktor Ulrich

Kyra Bothwell

EU FP7 GRAIL, EPSRC, ESF, QUILL partners, McClay Fund, CSC

Whole Cell Biocatalysis

Dr Martin Rebros, STU, Slovakia

Prof Gillian Stephens, Nottingham, UK

EPSRC X-ray and solid state NMR services, QUB technical and analytical services,

and you for listening